DOI: 10.1002/ejoc.201101485

# Synthesis and Two-Photon Properties of Small Dendritic Chromophores with Symmetrical and Unsymmetrical Substituted Skeletons

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**Keywords:** Dendritic chromophores / Two-photon absorption / Palladium-catalyzed amination

A set of novel multi-branched chromophores consisting of two groups of fluorene/oxadiazole-based analogues with generic skeletons of donor-π-acceptor (unsymmetrical) and donor-π-acceptor-π-donor (symmetrical) type has been synthesized and shown to display strong and broadly dispersed two-photon absorptivities in the near infrared (NIR) region on irradiation with femtosecond laser pulses. It is also demonstrated that structural parameters such as the number of donor units attached and the substitution pattern are closely connected to the molecular two-photon activities of these model compounds.

## Introduction

Two-photon absorption (2PA) occurs when a molecule is promoted from the ground state to an excited state through simultaneous absorption of two photons. Although the theory of this nonlinear optical phenomenon was predicted by Maria Göppert-Mayer in 1931,[1] experimental evidence was to appear only about thirty years later, with the observation of up-converted emission from media on irradiation with laser light of wavelengths far from the linear absorption bands of the studied media.[2] In the past fifteen years, the availability of stable and high-peak-power lasers has provided the momentum for exploration of two-photon technologies. Many potential applications based on 2PA in the emerging field of photonics and biophotonics have been proposed and explored, including optical power limiting, frequency-up-converted lasing, 3D data storage, 3D microfabrication, nondestructive bio-imaging and tracking, and two-photon-assisted photodynamic therapy.[3] For use in these applications, organic compounds that undergo large 2PA in desired spectral regions are consequently in great demand. So far, it has been established that molecular 2PA governed by combinations of several structural parameters such as intramolecular charge-transfer efficiency and/or effective size of π-conjugation domain within a molecule.[4–9] For various practical requirements, depending on the desired application, different photophysical properties in addition to strong molecular 2PA might also be required for the designed molecules. For utilization as, for instance, optical power limiters operating in the nanosecond regime, compounds with extended excited-state lifetimes might benefit the apparent nonlinear absorption because of two-photon-assisted excited-state absorption (2PA-assisted ESA)[10]

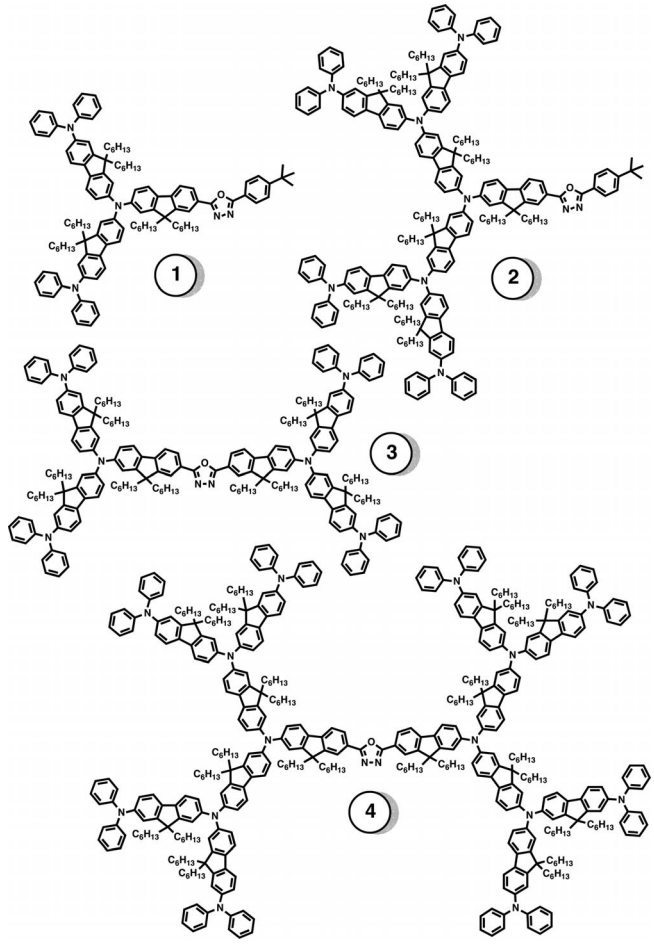


Figure 1. Molecular structures of the studied model chromophores.

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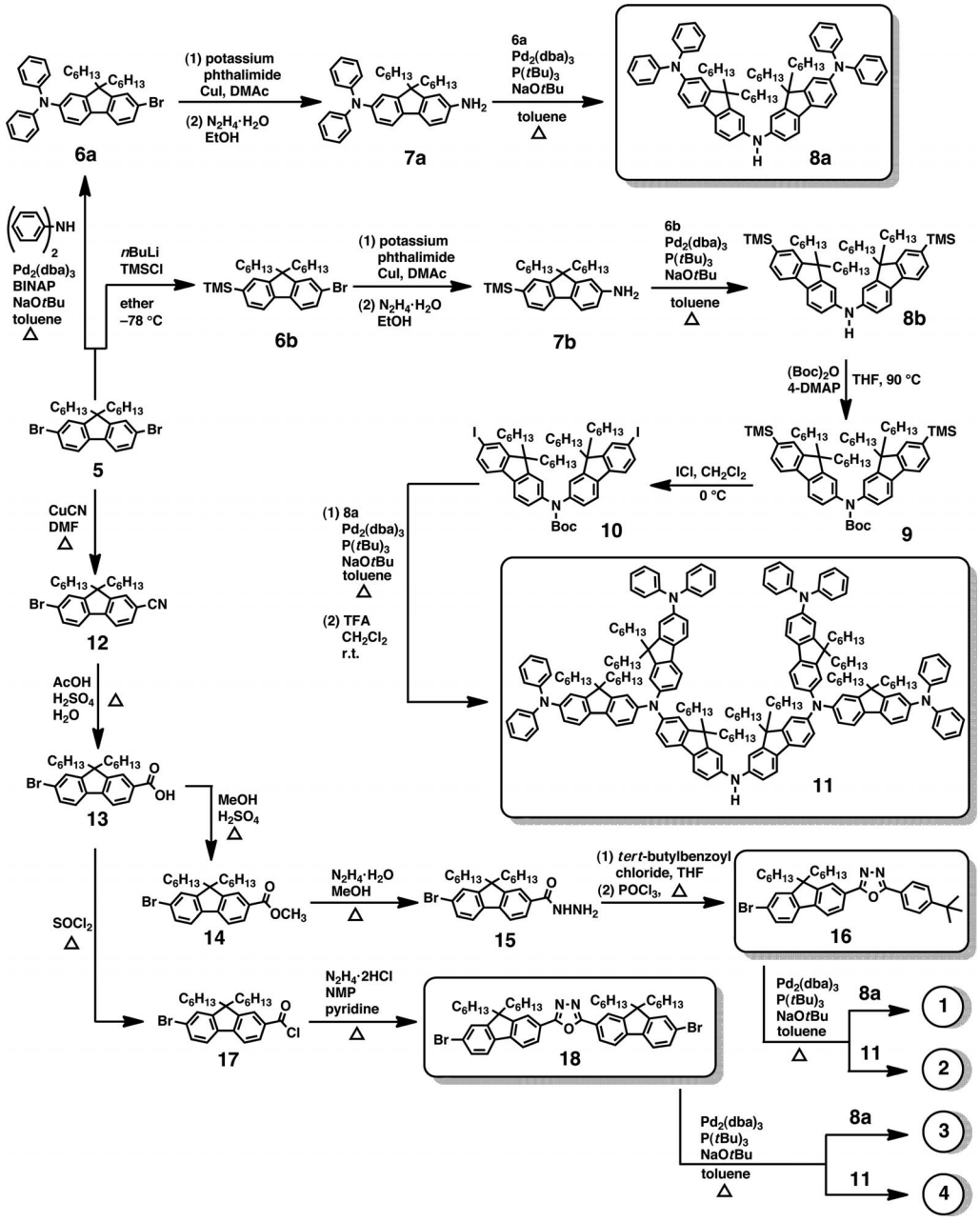
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101485.

so that their effective optical power restriction performances will be enhanced. In our investigations of the relationships between structural parameters and nonlinear absorption properties in conjugated systems, we were interested in exploring the influence of the arrangements of building units and substitution patterns on molecular 2PA in the construction of multi-branched π-frameworks. Here we present the synthesis of a new series of two-photon-active model chromophores (**1**–**4**; Figure 1) derived from functionalized fluorene and oxadiazole moieties, together with initial investigations of their 2PA properties in the femtosecond time domain.

## Results and Discussion

The chemical structures of the studied model compounds and the synthetic routes to them are illustrated in Figure 1 and Scheme 1, respectively. This model compound set contains four multi-branched congeners and can be categorized into two groups according to their substitution patterns. Compounds **1** and **2** have a generic donor-π-acceptor (D-π-A) structure based on the use of functionalized fluorene and oxadiazole units to construct their unsymmetrical skeletons, whereas model compounds **3** and **4** utilize the same building units to make up their symmetrical scaffolds with




Scheme 1. Synthetic routes to key intermediates (**8a**, **11**, **16**, and **18**) and model chromophores.

donor-π-acceptor-π-donor (D-π-A-π-D) backbone. In theory, the dumbbell-shaped structures of chromophores **3** and **4** can be regarded as *"dimerized"* versions of compounds **1** and **2**, respectively. The original design concept for these model compounds involved the tentative construction of a set of structurally symmetrical and unsymmetrical π-frameworks with various numbers of electron-donating units attached such that the resulting fluorophores might exhibit charge-transfer/redistribution in different manners upon light excitation. On the other hand, the pendent alkyl chains on all fluorenyl moieties in these model chromophores can be expected to enhance their solubilities in common organic solvents; this is an important parameter to consider in the molecular design from the aspects both of experiment and of applications. The synthetic procedures for these model dye molecules are relatively straightforward and mainly involve consecutive functionalization processes on the fluorene moiety followed by Buchwald–Hartwig-type amination to prepare the key intermediates and the final model compounds as shown in Scheme 1. The syntheses of these key intermediates and the final model chromophores are described in detail in the Experimental Section.

Figure 2 shows linear absorption and fluorescence spectra of the studied dye molecules in solution phase by using THF as the solvent. Intense one-photon absorption (1PA) of these compounds was found around 400 nm (with $\varepsilon_{max} \approx 1.01 \times 10^5$ cm$^{-1}$ M$^{-1}$ for **1**, $\varepsilon_{max} \approx 2.17 \times 10^5$ cm$^{-1}$ M$^{-1}$ for **2**, $\varepsilon_{max} \approx 1.70 \times 10^5$ cm$^{-1}$ M$^{-1}$ for **3**, and $\varepsilon_{max} \approx 3.70 \times 10^5$ cm$^{-1}$ M$^{-1}$ for **4**). These model chromophores also exhibit strong two-photon-excited up-conversion emission, which can be readily seen with the naked eye even on illumination with a ca. 790 nm unfocused femtosecond laser beam at low intensity level. Figure 3(a) shows the 2PA-induced fluorescence spectra of compounds **1**–**4**, and the curves in Figure 3(b)–(e) confirm that the 2PA process is responsible for the detected up-conversion emission in all cases. In order to probe and compare the dispersion of 2PA behavior of these dye molecules as a function of wavelength, we conducted degenerate two-photon-excited fluorescence (2PEF) measurement in the near-IR region (700–850 nm) with use of fluorescein (ca. 80 μM in NaOH solution, pH = 11) as the standard. Figure 4 shows the measured degenerate two-photon absorption spectra of these model compounds in THF, and the combined photophysical data are summarized in Table 1.

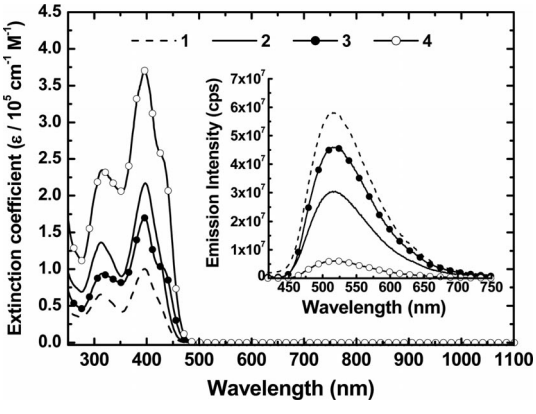



Figure 2. Linear absorption and fluorescence spectra (inset) of compounds **1**–**4** in solution phase ($1 \times 10^{-5}$ M in THF).

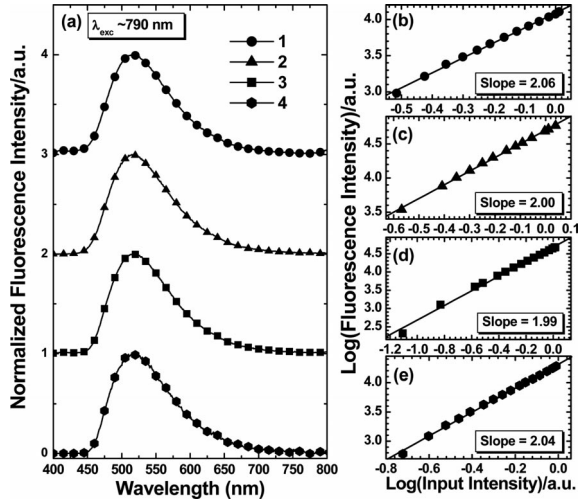



Figure 3. (a) Normalized two-photon excited up-conversion spectra of fluorophores **1**–**4** in THF at $1 \times 10^{-4}$ M. (b), (c), (d), (e) Logarithmic plots of power-squared dependences of the 2PA-induced fluorescence intensities on the input intensities of these compounds in THF.

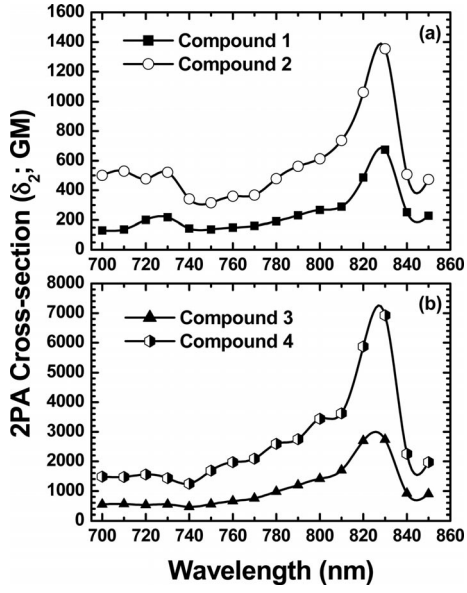



Figure 4. Measured degenerate two-photon absorption spectra of model chromophores **1**–**4** by the 2PEF method in THF solution at $1 \times 10^{-4}$ M (experimental error ca. ±15%).

With use of compound **1** as a reference point, it is notable from Figure 4 that all these model chromophores not only exhibit nearly identical dispersion patterns of their two-photon activities but also show ascending overall magnitude of 2PA from compound **1** to compound **4**. These features indicate that either simply increasing the number of attached electron-donating units (as in the case of compound **2**) or extending the size of the π-domain by construc-

Table 1. Photophysical properties of the studied model chromophores **1**–**4**.[a]

| | $\lambda_{max}^{abs}$ [nm][b] | $\log \varepsilon_{max}$ | $\lambda_{max}^{em}$ [nm][c] | $\Phi_F$[d] | $\tau_{1PA-FL}$ [ns][e] | $\delta_2^{max}$ [GM][f] | $N_\pi^{eff}$[g] | $\delta_2^{max}/N_\pi^{eff}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 396 | 5.00 | 518 | 0.40 | 3.25 | ca. 675 | 30.3 | ca. 22.3 |
| 2 | 397 | 5.34 | 519 | 0.43 | 3.27 | ca. 1350 | 40.4 | ca. 33.4 |
| 3 | 396 | 5.23 | 518 | 0.47 | 2.95 | ca. 2730 | 40.6 | ca. 67.2 |
| 4 | 396 | 5.57 | 518 | 0.51 | 2.95 | ca. 6930 | 55.6 | ca. 124.6 |

[a] Concentrations were $1 \times 10^{-5}$ M and $1 \times 10^{-4}$ M for 1PA-related and 2PA-related measurements, respectively. [b] One-photon absorption maxima. [c] 1PA-induced fluorescence emission maxima. [d] Fluorescence quantum efficiencies. [e] 1PA-induced fluorescence lifetimes. [f] Maximum 2PA cross-section values (experimental error ca. ±15%); 1 GM = $1 \times 10^{-50}$ cm$^4$ s/photon-molecule. [g] Effective π-electron numbers.

tion of a D-π-A-π-D scaffold based on the original D-π-A framework of compound **1** (as in the case of compound **3**) will enhance the molecular 2PA without shifting the major 2PA band in this dye system. Molecules with properties of this kind could be very beneficial for some particular applications when large multi-photon absorptivities in a specific spectral region are required. According to this line of design concept, the structure of model compound **4** represents a combination of the two previous structural motifs, and – because no deterioration in molecular 2PA was observed – it can be assumed that these two structural parameters are additive for the studied molecular system. Furthermore, the relative increment in the magnitude of the observed overall and maximum 2PA for these model chromophores (see Figure 4 and Table 1) suggests that extending the size of the π-system from the original D-π-A framework to a D-π-A-π-D skeleton provides a more effective approach to enhanced molecular 2PA. Additionally, it is notable that the excited-state lifetimes of the studied model chromophores in this work are in the nanosecond range, which suggests that a significant excited-state population can be retained and should consequently display excited-state absorption during excitation by longer laser pulses. This feature is particularly desirable in relation to optical power-limiting applications in the nanosecond regime based on 2PA-induced excited-state absorption (2PA-induced ESA), because the effective three-photon absorption coefficient increases significantly with the excited-state lifetime.[10f,10g] The power restriction performances of these compounds on subjection to nanosecond laser pulses are currently under investigation and will be reported in due course.

## Conclusions

We have synthesized a novel multipolar chromophore set consisting of four analogues with symmetrical and unsymmetrical substituted skeletons through the use of functionalized fluorene and oxadiazole moieties as the major building units. The initial experimental results indicate that these model fluorophores manifest strong and widely dispersed two-photon absorptivities in the near-IR region. Tentative analysis of the correlation between molecular structures and the observed overall 2PA behavior found that both increasing the number of electron-donating units and extending the size of the π-domain by construction of a D-π-A-π-D scaffold based on the original D-π-A framework will enhance the molecular 2PA without shifting the major 2PA band in this dye system. Moreover, the measured nanosecond excited-state lifetimes suggest that these model compounds could be potential candidates as broad-band optical power limiters for laser pulses with long duration.

## Experimental Section

**General:** All commercially available reagents for the preparation of the intermediates and targeted chromophores were obtained from Aldrich Chemical Co. and were used as received, unless stated otherwise. THF was distilled from sodium benzophenone ketyl. $^1$H and $^{13}$C NMR spectra were recorded either with 200 or 300 MHz spectrometers and referenced to TMS or residual $CHCl_3$. HRMS measurements were conducted with a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF mass spectra were obtained with a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA).

**Synthesis:** In Scheme 1, compound **5** (2,7-dibromo-9,9-dihexyl-9*H*-fluorene) is the major starting material for the synthesis of the backbone of each intermediate and model chromophore. This compound was obtained in a total yield of ca. 80% by bromination[1] and subsequent alkylation[2] of a fluorene unit. For the synthesis of other key intermediates and the targeted model compounds, a series of functionalization steps by starting from compound **5** were conducted.

**7-Bromo-9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (6a):** BINAP (1.14 g, 1.8 mmol), $Pd_2(dba)_3$ (0.56 g, 0.6 mmol), and sodium *tert*-butoxide (8.2 g, 0.084 mol) were added to a mixture of compound **5** (30 g, 0.06 mol) and diphenylamine (11.34 g, 0.067 mol) in toluene (120 mL), and the mixture was stirred at 80 °C under Ar for 24 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The above solution was then extracted with ethyl acetate and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with hexane as eluent to give the final purified product as a pale yellow oil in a yield of ca. 55% (19.44 g). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.54–7.50 (m, 1 H), 7.50–7.44 (d, $J$ = 8.1 Hz, 1 H), 7.45–7.40 (dd, $J_1$ = 8.1 Hz, $J_2$ = 3 Hz, 2 H), 7.30–7.22 (m, 4 H), 7.14–7.09 (dd, $J_1$ = 8.1 Hz, $J_2$ = 3 Hz, 2 H), 7.14–7.09 (m, 2 H), 7.05–6.98 (m, 4 H), 1.87–1.79 (m, 4 H), 1.17–0.99 (m, 12 H), 0.81 (t, $J$ = 7.04 Hz, 6 H), 0.64 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 152.79, 151.67, 147.82, 147.49, 139.88, 135.00, 129.87, 129.13, 125.89, 123.41, 122.85, 120.41, 122.58, 120.43, 120.36, 120.14, 119.01, 55.26, 40.10, 31.44, 29.51, 23.66, 22.50, 14.03 ppm. HRMS (FAB): calcd. for $C_{37}H_{42}BrN$ $[M]^+$ 579.2501; found 579.2507 $[(^{79}Br)M]^+$, 581.2483 $[(^{81}Br)M]^+$.

**9,9-Dihexyl-$N^2$,$N^2$-diphenyl-9*H*-fluorene-2,7-diamine(7a):** Two-step reaction. (*i*) Potassium phthalimide (4.77 g, 0.258 mol) and CuI (4.92 g, 0.258 mol) were added to a solution of compound **6a** (15 g, 0.258 mol) in DMAc (135 mL). The resulting solution was stirred and heated at reflux for 24 h. After the mixture had cooled to room temperature, it was extracted with diethyl ether and then dried with $MgSO_4$. After removal of the solvent, the crude product was obtained as dark brown solid. (*ii*) $NH_2NH_2{\cdot}H_2O$ (1.293 g, 0.258 mol) was added to a solution of the crude product from the first step in ethanol (150 mL). The resulting solution was stirred and heated at reflux for 6 h. After the mixture had cooled to room temperature, it was extracted with ethyl acetate (3 × 30 mL) and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with diethyl ether/hexane (1:10) as eluent to give the final purified product in a yield of ca. 62% (8.31 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.43–7.40 (t, $J$ = 7.2 Hz, 2 H), 7.23–7.18 (t, $J$ = 7.2 Hz, 4 H), 7.11–7.07 (m, 5 H), 7.00–6.92 (m, 3 H), 6.61–6.59 (m, 2 H), 3.689–3.66 (s, 2 H), 1.87–1.79 (m, 4 H), 1.17–0.99 (m, 12 H), 0.81 (t, $J$ = 8.4 Hz, 6 H), 0.64 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 152.51, 151.09, 148.08, 145.38, 137.25, 132.15, 128.96, 124.03, 123.22, 121.93, 119.97, 119.89, 118.89, 113.87, 109.68, 54.72, 40.42, 31.46, 29.60, 23.65, 22.49, 13.97 ppm. HRMS (FAB): calcd. for $C_{37}H_{44}N_2$ $[M]^+$ 516.3504; found 516.3505.

**$N^2$-[7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]-9,9-dihexyl-$N^7$,$N^7$-diphenyl-9*H*-fluorene-2,7-diamine (8a):** $Pd_2(dba)_3$ (0.073 g, 0.0803 mmol), sodium *tert*-butoxide (1.852 g, 0.193 mol), and P(*t*Bu)$_3$ (0.0322 g, 0.161 mmol) were added to a mixture of compounds **7a** (8.3 g, 0.161 mol) and **6a** (9.3 g, 0.161 mol) in dry toluene (15 mL), and the mixture was stirred at 90 °C under Ar for 12 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The solution was then extracted with ethyl acetate (3 × 30 mL) and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with diethyl ether/hexane (1:20) as eluent to give the final purified product in a yield of ca. 60.2% (4.91 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.26–7.20 (t, $J$ = 8.1 Hz, 12 H), 7.12–7.10 (t, $J$ = 8.1 Hz, 12 H), 7.02–6.95 (m, 8 H), 5.01 (s, 1 H), 1.84–1.79 (m, 4 H), 1.15–1.08 (m, 12 H), 0.81 (t, 6 H), 0.64 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 148.06, 134.28, 132.46, 131.23, 129.03, 127.06, 123.83, 123.60, 123.44, 122.53, 122.14, 54.91, 40.43, 31.54, 29.68, 23.80, 22.54, 13.98 ppm. HRMS: $[M]^+$ calcd. for $C_{74}H_{85}N_3$ 1015.6743; found 1015.6738.

**(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)trimethylsilane (6b):** *n*-Butyllithium in hexane (26.9 mL, 1.6 M, 0.043 mol) was added at –78 °C under $N_2$ to a solution of **5** (20 g, 0.041 mol) in dry diethyl ether (150 mL), and the mixture was stirred for 1 h. Chlorotrimethylsilane (6 mL, 0.0462 mol) was added slowly at –78 °C, and the reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The reaction mixture was quenched with saturated brine, and the resulting solution was extracted with diethyl ether. The organic layer was washed with brine and $H_2O$ three times and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by chromatography on silica with hexane as eluent to give the final purified product as a colorless oil (19.16 g, 97%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.85–7.84 (d, $J$ = 7.8 Hz, 1 H), 7.77–7.73 (m, 2 H), 7.63–7.61 (m, 2 H), 7.54–7.52 (d, $J$ = 7.8 Hz, 1 H), 2.13–2.12 (m, 4 H), 1.20–1.19 (m, 12 H), 0.91 (t, $J$ = 7.8 Hz, 6 H), 0.64 (m, 4 H), 0.46 (s, 9 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 153.26, 153.07, 149.39, 149.17, 140.68, 139.71, 136.03, 132.09, 129.89, 127.41, 126.19, 121.44, 122.32, 121.07, 119.06, 55.20, 40.03, 31.30, 29.50, 23.57, 22.45, 14.00, –0.89 ppm. HRMS (FAB): calcd. for $C_{28}H_{41}BrSi$ $[M]^+$ 484.2161; found 484.2150 $[(^{79}Br)M]^+$, 486.2164 $[(^{81}Br)M]^+$.

**9,9-Dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-amine (7b):** Two-step reaction. (*i*) Potassium phthalimide (7.26 g, 0.039 mol), and CuI (7.44 g, 0.039 mol) were added to a solution of compound **6b** (19 g, 0.039 mol) in DMAc (45 mL), and the mixture was stirred and heated at reflux for 24 h. After the mixture had cooled to room temperature, it was extracted with diethyl ether and dried with $MgSO_4$. After removal of the solvent, the crude product was obtained as brown solid. (*ii*) $NH_2NH_2{\cdot}H_2O$ (2.46 g, 0.039 mol) was added to a solution of the crude product from the first step in ethanol (300 mL), and the resulting solution was stirred and heated at reflux for 6 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with diethyl ether/hexane (1:10) as eluent to give the final purified product in a yield of 70.5% (11.62 g). HRMS (FAB): calcd. for $C_{28}H_{43}NSi$ $[M]^+$ 421.3165; found 421.7332.

**Bis[9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl]amine (8b):** $Pd_2(dba)_3$ (0.0976 g, 0.1064 mmol), sodium *tert*-butoxide (2.48 g, 0.256 mol), and P(*t*Bu)$_3$ (0.044 g, 0.2132 mmol) were added to a mixture of compound **7b** (9 g, 0.0213 mol) and **6b** (10.36 g, 0.0213 mol) in dry toluene (60 mL), and the mixture was stirred at 90 °C under Ar for 12 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The above solution was then extracted with ethyl acetate (3 × 30 mL) and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:40) as eluent to give the final purified product in a yield of 55.6% (4.9 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.59–7.56 (m, 6 H), 7.47–7.43 (m, 6 H), 2.02–2.01 (m, 8 H), 1.14–1.12 (m, 24 H), 0.79–0.75 (m, 12 H), 0.30 (m, 8 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 152.44, 152.14, 149.21, 141.93, 137.35, 134.38, 131.82, 127.31, 120.70, 118.05, 116.85, 111.64, 54.88, 40.45, 31.46, 29.71, 23.73, 22.55, 14.01 ppm. HRMS: calcd. for $C_{56}H_{83}NSi_2$ $[M]^+$ 825.6064; found 825.6063.

***tert*-Butyl Bis[9,9-dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl]carbamate (9):** $(Boc)_2O$ (2.59 g, 0.012 mol) and 4-DMAP (0.362 g, 0.003 mmol) were added to a mixture of compound **8b** (4.9 g, 6 mmol) in dry THF (45 mL), and the mixture was stirred at 90 °C under $N_2$ for 12 h. After the mixture had cooled to room temperature, it was extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:50) as eluent to give the final purified product in a yield of ca. 81% (4.45 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.64 (t, $J$ = 7.8 Hz, 4 H), 7.54–7.52 (d, $J$ = 8.1 Hz, 2 H), 7.29–7.28 (d, $J$ = 8.1 Hz, 2 H), 7.24–7.21 (d, $J$ = 7.8 Hz, 2 H), 2.02–1.95 (m, 8 H), 1.11–1.16 (m, 24 H), 0.85–0.76 (m, 12 H), 0.68 (m, 8 H), 0.36 (s, 9 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 153.75, 152.11, 151.27, 149.98, 142.64, 141.20, 138.65, 138.33, 131.79, 127.35, 125.16, 121.75, 119.79, 118.82, 80.86, 54.93, 40.12, 31.38, 29.55, 28.28, 23.62, 22.46, 13.98 ppm. HRMS: calcd. for $C_{56}H_{83}NSi_2$ $[M]^+$ 925.6588; found 925.6487.

***tert*-Butyl Bis(9,9-dihexyl-7-iodo-9*H*-fluoren-2-yl)carbamate (10):** Iodine monochloride (1.64 g, 0.01 mol) was added at 0 °C to a solution of compound **9** (4.45 g, 0.048 mol) in $CH_2Cl_2$ (20 mL). The resulting solution was then allowed to warm to room temperature and stirred for 4 h, after which saturated $NaHSO_3$ solution (ca. 50 mL) was added. The reaction mixture was extracted with dichloromethane (3 × 30 mL) and then dried with $MgSO_4$. After

removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:40) as eluent to give the final purified product in a yield of ca. 75% (3.72 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.68–7.62 (t, 4 H), 7.52–7.51 (d, 2 H), 7.29–7.28 (d, 2 H), 7.24–7.22 (d, 2 H), 1.81–1.78 (m, 8 H), 1.10–1.05 (m, 24 H), 0.84–0.76 (m, 12 H), 0.65 (m, 8 H), 0.368 (s, 9 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 152.75, 151.11, 150.87, 149.87, 141.54, 141.10, 138.95, 137.25, 130.24, 128.91 124.56, 120.25, 118.59, 118.26, 92.18, 80.88, 54.89, 39.84, 31.26, 29.48, 28.18, 22.89, 21.83 12.85 ppm. HRMS: calcd. for $C_{55}H_{73}I_2NO_2$ $[M]^+$ 1033.3731; found 1033.8998.

**$N^2$-[7-(7-{Bis[7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]-amino}-9,9-dihexyl-9*H*-fluoren-2-ylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]-$N^2$-[7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]-9,9-dihexyl-$N^7$,$N^7$-diphenyl-9*H*-fluorene-2,7-diamine (11):** Two-step reaction. (*i*) $Pd_2(dba)_3$ (0.085 g, 0.093 mmol), sodium *tert*-butoxide (0.468 g, 4.874 mmol), and P(*t*Bu)$_3$ (0.038 g, 0.186 mmol) were added to a mixture of compound **10** (2.4 g, 2.321 mol) and compound **8a** (4.718 g, 4.642 mol) in dry toluene (15 mL), and the mixture was stirred at 90 °C under Ar for 12 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The above solution was extracted with ethyl acetate (3 × 30 mL) and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:20) as eluent to give the final purified product in a yield of ca. 78% (5.08 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.61–7.39 (m, 12 H), 7.25–6.95 (m, 64 H), 1.85–1.80 (m, 24 H), 1.09–1.08 (m, 72 H), 0.82–0.78 (m, 36 H), 0.65 (m, 24 H), 0.368 (s, 9 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 152.79, 151.67, 147.82, 147.49, 139.88, 135.00, 129.87, 129.13, 125.89, 123.41, 122.85, 120.41, 122.58, 120.43, 120.36, 120.14, 119.01, 80.98, 55.26, 40.10, 31.44, 29.51, 23.66, 22.50, 14.03 ppm. HRMS: calcd. for $C_{203}H_{242}N_7O$ $[M + H]^+$ 2811.1313; found 2812.8954. (*ii*) TFA (1.44 g, 0.013 mol) was added to a solution of the compound from the first step in $CH_2Cl_2$ (30 mL), and the mixture was stirred at room temperature under Ar for 2 h. $NaOH_{(aq.)}$ (ca. 50 mL) was then added, and the mixed solution was extracted with dichloromethane (3 × 30 mL) and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:20) as eluent to give the final purified product in a yield of 84.6% (4.17 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.52–7.49 (m, 12 H), 7.25–7.20 (m, 20 H), 7.13–7.10 (d, $J$ = 8.4 Hz, 24 H), 7.01–6.95 (m, 20 H), 5.98 (s, 1 H), 2.04–1.82 (m, 24 H), 1.25–1.23 (m, 72 H), 0.80–0.78 (m, 36 H), 0.65 (m, 24 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 152.83, 151.89, 147.21, 147.05, 139.22, 135.28, 130.85, 129.83, 124.81, 123.41, 122.85, 120.29, 122.37, 120.51, 120.36, 120.14, 119.01, 55.26, 40.10, 31.44, 29.51, 23.66, 22.50, 14.03 ppm. HRMS: calcd. for $C_{198}H_{234}N_7$ $[M + H]^+$ 2712.0155; found 2712.0996.

**7-Bromo-9,9-dihexyl-9*H*-fluorene-2-carbonitrile (12):** CuCN (1.3 g, 14.6 mmol) was added to a mixture of compound **5** (8 g, 0.016 mol) and dry DMF (50 mL), and the mixture was stirred at 110 °C for 24 h. After the mixture had cooled to room temperature, $NaOH_{(aq.)}$ (ca. 50 mL) was added. The above solution was extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:20) as eluent to give the final purified product in a yield of ca. 45% (3.21 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.75–7.72 (dd, 1 H), 7.65–7.58 (m, 3 H), 7.52–7.49 (m, 2 H), 2.00–1.90 (m, 4 H), 1.15–1.03 (m, 12 H), 0.88–0.75 (m, 6 H), 0.61–0.49 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 153.46, 150.99, 144.51, 138.08, 131.40, 130.51, 126.44, 126.38, 123.17, 122.09, 120.29, 119.59, 110.34, 55.75, 39.95, 31.36, 29.42, 23.60, 22.46, 13.90 ppm. HRMS: calcd. for $C_{26}H_{33}BrN$ 438.1718 $[M + H]^+$; found $[(^{79}Br)M + H]^+$ = 438.1794; $[(^{81}Br)M + H]^+$ = 440.1794.

**7-Bromo-9,9-dihexyl-9*H*-fluorene-2-carboxylic Acid (13):** A mixture of compound **12** (2.7 g, 0.006 mol) in $CH_3COOH$ (6 mL), $H_2SO_4$ (6 mL), and $H_2O$ (6 mL) was stirred and heated at reflux for 24 h. After the mixture had cooled to room temperature, $NaOH_{(aq.)}$ (ca. 50 mL) was added. The above mixed solution was extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) as eluent to give the final purified product in a yield of ca. 97% (2.73 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.17, 8.14 (d, $J$ = 7.5 Hz, 1 H), 8.10 (s, 1 H), 7.77, 7.74 (d, $J$ = 7.5 Hz, 1 H), 7.64, 7.61 (d, $J$ = 8.1 Hz, 1 H), 7.52–7.48 (m, 2 H), 2.16–1.91 (m, 4 H), 1.14–1.05 (m, 12 H), 0.78–0.74 (t, 6 H), 0.59 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 172.68, 154.10, 150.51, 145.61, 138.74, 130.31, 129.75, 128.10, 126.39, 124.60, 122.77, 122.06, 119.62, 55.61, 40.08, 31.43, 29.54, 23.68, 22.52, 13.95 ppm. HRMS: calcd. for $C_{26}H_{34}BrO_2$ $[M + H]^+$ 457.1664; found 457.1751 $[(^{79}Br)M + H]^+$, 459.1799 $[(^{81}Br)M + H]^+$.

**Methyl 7-Bromo-9,9-dihexyl-9*H*-fluorene-2-carboxylate (14):** A mixture of compound **13** (2.6 g, 5.6 mmol) in methanol (20mL) and $H_2SO_4$ (4 mL) was stirred and heated at reflux for 6 h. After the mixture had cooled to room temperature, $NaOH_{(aq.)}$ (ca. 50 mL) was added. The above mixed solution was extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:20) as eluent to give the final purified product in a yield of ca. 93% (2.49 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.06–8.02 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.2 Hz, 1 H), 7.99 (s, 1 H), 7.71, 7.68 (d, $J$ = 7.8 Hz, 1 H), 7.61, 7.58 (d, $J$ = 7.8 Hz, 1 H), 7.49–7.46 (m, 2 H), 3.95 (s, 3 H), 2.06–1.88 (m, 4 H), 1.13–1.01 (m, 12 H), 0.78–0.73 (t, $J$ = 6.9 Hz, 6 H), 0.61–0.51 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 167.31, 153.91, 150.35, 144.61, 138.86, 130.17, 128.90, 126.30, 123.99, 122.40, 121.83, 119.42, 55.53, 52.03, 40.05, 31.37, 29.48, 23.60, 22.45, 13.86 ppm. HRMS: calcd. for $C_{27}H_{36}BrO_2$ 471.182 $[M + H]^+$; found 471.1900 $[(^{79}Br)M + H]^+$, 473.1921 $[(^{81}Br)M + H]^+$.

**7-Bromo-9,9-dihexyl-9*H*-fluorene-2-carbohydrazide (15):** $NH_2NH_2 \cdot H_2O$ (0.637 g, 0.01 mol) was added to a mixture of compound **14** (2.4 g, 5.1 mmol) in methanol (20mL), and the resulting solution was then stirred and heated at reflux for 24 h. The reaction mixture was extracted with dichloromethane (3 × 30 mL) and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) as eluent to give the final purified product in a yield of 91.6% (2.28 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.05 (s, 1 H), 7.84–7.74 (m, 2 H), 7.70, 7.67 (d, $J$ = 7.8 Hz, 1 H), 7.59, 7.56 (d, $J$ = 7.8 Hz, 1 H), 7.49 (s, 1 H), 4.24 (s, 3 H), 2.10–1.86 (m, 4 H), 1.12–1.01 (m, 12 H), 0.77–0.72 (t, $J$ = 6.6 Hz, 6 H), 0.65–0.51 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 168.79, 153.56, 150.83, 143.69, 138.76, 131.30, 130.17, 126.26, 125.76, 122.27, 121.74, 121.66, 119.68, 55.60, 40.09, 31.37, 29.48, 23.62, 22.45, 13.87 ppm. HRMS: calcd. for $C_{26}H_{36}BrN_2O$ $[M + H]^+$ 471.1933; found 471.2009 $[(^{79}Br)M + H]^+$, 473.2011 $[(^{81}Br)M + H]^+$.

**2-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (16):** Two-step reaction. (*i*) 4-*tert*-Butylbenzoyl chloride (1.03 g, 5.2 mmol) and pyridine (3 mL) were added to a mixture of compound **15** (2.25 g, 4.7 mmol) and THF (60 mL), and the resulting mixed solution was heated (ca. 60 °C) and stirred for 12 h. After the mixture had cooled to room temperature, the sol-

vent was removed by filtration, and the crude solid product was collected and recrystallized from hexane. The purified product was obtained as a white powder in a yield of 90.3% (2.72 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 10.16, 10.14 (d, $J$ = 7.2 Hz, 1 H), 9.81, 9.79 (d, $J$ = 7.2 Hz, 1 H), 7.96–7.92 (m, 2 H), 7.85, 7.82 (d, $J$ = 7.5 Hz, 2 H), 7.69, 7.66 (d, $J$ = 7.5 Hz, 1 H), 7.57, 7.54 (d, $J$ = 7.5 Hz, 1 H), 7.48–7.43 (m, 4 H), 1.95–1.89 (m, 4 H), 1.32 (s, 9 H), 1.11–0.93 (m, 12 H), 0.74–0.68 (t, $J$ = 6.9 Hz, 6 H), 0.50 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 164.73, 164.36, 156.09, 153.77, 150.87, 144.26, 138.80, 130.22, 130.14, 128.44, 127.17, 126.91, 126.33, 125.70, 122.43, 121.84, 121.79, 119.84, 55.72, 40.12, 35.02, 31.45, 31.09, 29.52, 23.70, 22.52, 13.93 ppm. HRMS: calcd. for $C_{37}H_{48}BrN_2O_2$ $[M + H]^+$ 631.2821; found 631.2908 $[(^{79}Br)M + H]^+$, 633.2911 $[(^{81}Br)M + H]^+$. (*ii*) A mixture of the compound from the first step and $POCl_3$ (45 mL) was stirred and heated at ca. 90 °C for 6 h. After the mixture had cooled to room temperature, it was poured into ice/water (ca. 50 mL) and stirred for 30 min. After filtration, the crude solid product was collected and recrystallized from methanol. The purified product was obtained as a white powder in a yield of ca. 79% (2.09 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.14–8.09 (m, 4 H), 7.80, 7.78 (d, $J$ = 8.1 Hz, 1 H), 7.62–7.47 (m, 5 H), 2.13–1.94 (m, 4 H), 1.37 (s, 9 H), 1.14–1.05 (m, 12 H), 0.77–0.72 (t, $J$ = 7.2 Hz, 6 H), 0.65–0.60 (m, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 164.76, 164.49, 155.18, 153.47, 151.13, 143.43, 138.80, 130.23, 126.70, 126.24, 126.02, 125.94, 122.72, 122.35, 121.65, 121.19, 121.07, 120.20, 55.69, 40.12, 34.97, 31.37, 31.02, 29.46, 23.63, 22.44, 13.87 ppm. HRMS: calcd. for $C_{37}H_{45}BrN_2O$ $[M]^+$ 612.2715; found 612.2709 $[(^{79}Br)M + H]^+$, 614.2722 $[(^{81}Br)M + H]^+$.

**7-Bromo-9,9-dihexyl-9*H*-fluorene-2-carbonyl Chloride (17):** A mixture of compound **13** (6.4 g, 0.014 mol) and thionyl chloride (70mL), was stirred and heated at reflux under Ar for 12 h. After the mixture had cooled to room temperature, the solvent was evaporated under low pressure. The crude product was obtained in a yield of ca. 89% (5.93 g) and was used for the next step without further purification.

**2,5-Bis(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-1,3,4-oxadiazole (18):** Two-step reaction. (*i*) $N_2H_4$·2HCl (0.653 g, 0.006 mol) and pyridine (15 mL) were added to a mixture of compound **17** (5.92 g, 0.012 mol) and NMP (50 mL), and the resulting mixture was then stirred at 50 °C for 12 h. After the mixture had cooled to room temperature, it was poured into ice/water (50 mL). The crude solid product was collected by filtration and recrystallized from ethyl acetate/methanol. The purified product was obtained as a brown powder in a yield of 60.3% (3.41 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.34 (s, 2 H), 7.89 (s, 2 H), 7.87–7.86 (m, 2 H), 7.78, 7.75 (d, $J$ = 7.2 Hz, 2 H), 7.64, 7.61 (d, $J$ = 7.8 Hz, 2 H), 7.51–7.49 (m, 4 H), 2.04–1.94 (m, 8 H), 1.14–1.03 (m, 24 H), 0.78–0.74 (t, $J$ = 6.6 Hz, 12 H), 0.59–0.54 (m, 8 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 164.74, 153.72, 150.90, 144.41, 138.69, 130.25, 129.94, 126.94, 126.31, 122.52, 121.80, 119.90, 55.70, 40.10, 31.43, 29.52, 23.68, 22.51, 13.93 ppm. HRMS: calcd. for $C_{52}H_{67}Br_2N_2O_2$ $[M + H]^+$ 909.3491; found 909.3497 $[(^{79,79}Br)M + H]^+$, 911.3495 $[(^{79,81}Br)M + H]^+$, 913.3547 $[(^{81,81}Br)M + H]^+$. (*ii*) A mixture of the compound from the first step and $POCl_3$ (25 mL) was stirred and heated at reflux for 6 h. After the mixture had cooled to room temperature, it was poured into ice/water (50 mL). The above solution was then extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) as eluent to give the final purified product in a yield of ca. 91.2% (3.04 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.16–8.13 (m, 4 H), 7.84, 7.81 (d, $J$ = 7.2 Hz, 2 H), 7.65, 7.62 (d, $J$ = 7.2 Hz, 2 H), 7.52–7.49 (m, 4 H), 2.14–1.95 (m, 8 H), 1.17–0.99 (m, 24 H), 0.78–0.73 (t, 12 H), 0.66–0.59 (m, 8 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 165.00, 153.54, 151.25, 143.61, 138.83, 130.30, 126.32, 126.16, 122.68, 122.46, 121.72, 121.32, 120.26, 55.78, 40.17, 31.42, 29.50, 23.68, 22.47, 13.91 ppm. HRMS: calcd. for $C_{52}H_{65}Br_2N_2O$ $[M + H]^+$ 891.3385; found 891.3464 $[(^{79,79}Br)M + H]^+$, 893.3422 $[(^{79,81}Br)M + H]^+$, 895.3465 $[(^{81,81}Br)M + H]^+$.

**Compound 1:** $Pd_2(dba)_3$ (9.55 mg, 0.011 mmol), sodium *tert*-butoxide (0.06 g, 0.626 mmol), and P($t$Bu)$_3$ (4.2 mg, 0.021 mmol) were added to a mixture of compound **16** (0.32 g, 0.521 mmol) and compound **8a** (0.53 g, 0.521 mmol) in dry toluene (15 mL), and the resulting mixture was stirred at 90 °C under Ar for 12 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The above solution was then extracted with ethyl acetate and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) as eluent to give the final purified product in a yield of 80.6% (0.65 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.11–8.06 (m, 4 H), 7.73, 7.70 (d, $J$ = 7.8 Hz, 1 H), 7.59–7.54 (m, 3 H), 7.50–7.47 (d, $J$ = 7.8 Hz, 4 H), 7.26–7.21 (m, 12 H), 7.12–7.09 (d, $J$ = 7.8 Hz 10 H), 7.06–6.96 (m, 8 H), 2.06–1.76 (m, 12 H), 1.38 (s, 9 H), 1.19–1.07 (m, 36 H), 0.84–0.71 (m, 30 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 165.16, 164.38, 155.14, 152.74, 151.94, 151.86, 151.15, 148.32, 148.00, 146.49, 146.16, 144.73, 136.26, 136.21, 133.99, 129.10, 126.75, 126.00, 123.81, 123.61, 123.41, 122.32, 122.12, 121.22, 121.04, 119.74, 119.54, 119.22, 118.61, 116.93, 115.11, 55.06, 40.18, 35.06, 31.66, 31.12, 29.65, 23.92, 22.57, 14.09 ppm. HRMS: calcd. for $C_{111}H_{129}N_5O$ $[M]^+$ 1548.0197; found 1548.0194.

**Compound 2:** $Pd_2(dba)_3$ (3 mg, 0.003 mmol), sodium *tert*-butoxide (0.018 g, 0.1955 mmol), and P($t$Bu)$_3$ (1.3 mg, 0.006518 mmol) were added to a mixture of compound **16** (0.1 g, 0.163 mmol) and compound **11** (0.44 g, 0.163 mmol) in dry toluene (15 mL), and the resulting reaction mixture was stirred at 90 °C under Ar for 12 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The above mixed solution was extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:15) as eluent to give the final purified product in a yield of 73.1% (0.386 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.11–8.07 (m, 8 H), 7.73, 7.70 (d, $J$ = 8.1 Hz, 2 H), 7.60–7.55 (m, 8 H), 7.51, 7.48 (d, $J$ = 8.1 Hz, 8 H), 7.27–7.22 (m, 28 H), 7.13–7.10 (m, 18 H), 7.07–6.97 (m, 14 H), 2.06–1.77 (m, 28 H), 1.38 (s, 9 H), 1.17–1.08 (m, 84 H), 0.85–0.75 (m, 70 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 165.13, 164.33, 155.09, 152.70, 151.90, 151.81, 151.10, 148.28, 147.95, 146.45, 146.11, 144.70, 136.22, 136.16, 135.65, 133.95, 129.65, 129.06, 126.71, 125.97, 123.75, 123.57, 122.28, 121.20, 121.02, 119.76, 119.49, 119.20, 118.56, 116.87, 55.02, 40.15, 35.02, 31.62, 31.08, 29.62, 23.88, 22.54, 14.06 ppm. HRMS: calcd. for $C_{235}H_{278}N_9O$ $[M + H]^+$ 3244.77; found 3244.8767.

**Compound 3:** $Pd_2(dba)_3$ (3 mg, 0.00326 mmol), sodium *tert*-butoxide (0.145 g, 1.5 mmol), and P($t$Bu)$_3$ (0.01 g, 0.05 mmol) were added to a mixture of compound **18** (0.56 g, 0.6271 mmol) and compound **8a** (0.44 g, 1.254 mmol) in dry toluene (15 mL), and the mixture was stirred at 90 °C under Ar for 12 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The above solution was extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ether/hexane (1:8) as eluent to give the final purified product in a yield of 79.4% (0.386 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.15–8.10 (m, 4 H),

7.74, 7.72 (d, $J$ = 8.1 Hz, 2 H), 7.61, 7.58 (d, $J$ = 8.1 Hz, 2 H), 7.50, 7.47 (d, $J$ = 7.8 Hz, 8 H), 7.27–7.22 (m, 26 H), 7.13–7.07 (m, 18 H), 7.03–9.67 (m, 16 H), 2.08–1.76 (m, 24 H), 1.20–1.08 (m, 72 H), 0.85–0.72 (m, 60 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 165.12, 152.73, 151.94, 151.85, 151.16, 148.31, 148.00, 146.49, 146.16, 144.69, 136.21, 134.02, 129.09, 126.14, 123.81, 123.60, 123.40, 122.31, 121.30, 121.06, 119.78, 119.55, 118.60, 116.95, 55.06, 40.18, 31.66, 29.65, 23.92, 22.56, 14.08 ppm. HRMS: calcd. for $C_{200}H_{233}N_8O$ $[M + H]^+$ 2765.0351; found 2765.1206.

**Compound 4:** $Pd_2(dba)_3$ (3 mg, 0.00326 mmol), sodium *tert*-butoxide (0.019 g, 0.196 mmol), and P(*t*Bu)$_3$ (1.3 mg, 0.007 mmol) were added to a mixture of compound **16** (0.074 g, 0.083 mmol) and compound **11** (0.45 g, 0.166 mmol) in dry toluene (15 mL), and the resulting mixed solution was stirred at 90 °C under Ar for 12 h. After the mixture had cooled to room temperature, $H_2O$ (ca. 100 mL) was added. The above solution was extracted with ethyl acetate and then dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:30) as eluent to give the final purified product in a yield of ca. 50% (0.386 g). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.15–8.10 (m, 8 H), 7.74, 7.72 (d, $J$ = 7.8 Hz, 4 H), 7.61, 7.58 (d, $J$ = 7.8 Hz 4 H), 7.51, 7.48 (d, $J$ = 7.8 Hz, 16 H), 7.72–7.22 (m, 56 H), 7.13–7.10 (m, 42 H), 7.05–6.97 (m, 34 H), 2.08–1.76 (m, 56 H), 1.25–1.08 (m, 168 H), 0.86–0.72 (m, 140 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 165.12, 152.75, 151.95, 151.86, 151.17, 148.34, 148.00, 146.50, 146.18, 144.69, 136.27, 136.21, 134.02, 129.09, 126.13, 123.81, 123.61, 123.44, 122.32, 121.31, 121.03, 119.79, 119.55, 119.22, 118.63, 116.96, 55.06, 40.18, 31.65, 29.64, 23.92, 22.55, 14.07 ppm. HRMS: calcd. for $C_{448}H_{529}N_{16}O$ $[M + H]^+$ 6149.1757; found 6149.0358.

**Supporting Information** (see footnote on the first page of this article): Optical experiment details.

## Acknowledgments

We thank the National Science Council (NSC), Taiwan for financial support.

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Received: October 12, 2011
Published Online: February 8, 2012

  